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STUDY OF THE PROCESS OF THERMAL DECOMPOSITION OF PAN

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FIBER DURING HEAT TR (U) FOREIGN TECHNOLOGY DIV

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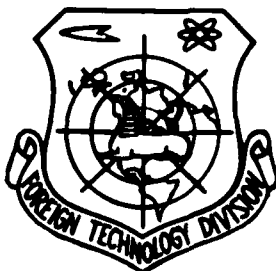
FOREIGN TECHNOLOGY DIVISION



STUDY OF THE PROCESS OF THERMAL DECOMPOSITION OF PAN FIBER DURING HEAT TREATMENT UP TO 1600°

by

A.S. Fialkov, O.F. Kuchinskaya, et al.



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Foreign page numbers occur in the English text and may be found anywhere along the left margin of the page as in this example:

In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.

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However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all cellular elements of the retina.

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З э	<i>З э</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after Ъ, Ь; e elsewhere.
When written as ѣ in Russian, transliterate as yѣ or ѣ.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	\sinh^{-1}
cos	cos	ch	cosh	arc ch	\cosh^{-1}
tg	tan	th	tanh	arc th	\tanh^{-1}
ctg	cot	cth	coth	arc cth	\coth^{-1}
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian English

rot curl
lg log

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STUDY OF THE PROCESS OF THERMAL DECOMPOSITION OF PAN¹FIBER DURING HEAT TREATMENT UP TO 1600°.

FOOTNOTE ¹. Polyacrylonitrile. ENDFOOTNOTE.

A.S. Fialkov, O. F. Kuchinskaya, S. G. Zaychikov, V. A. Kabardina.

In series/number of works, dedicated to question of obtaining carbon graphite fibers on basis PAN, their physicommechanical properties are described, results of analyses of structural and chemical transformations of initial material during its heat treatment [1-7] are given. The region of the low-temperature pyrolysis, realized predominantly in the vacuum or in inert atmosphere, is most investigated. Keywords: Polyacrylonitrile; Russian translations

It is known [3, 4], that structure PAN undergoes during heat processing/treatment of changes, which lead to obtaining of polymer, which consists in essence of condensed pyridine cycles with with conjugated bonds C=C and C=N. During the heating of PAN in the vacuum or in the inert gas first of all are formed the C=N-conjugated bonds. However, there are indications [5] that the low-temperature treatment in air already at 150° can lead to the formation of the C=C-conjugated bonds.

In the present work study is undertaken of the process of thermal decomposition of PAN fibers with heat treatment up to 1600° with utilization of isothermal holdings in air at 200 and 235° for purpose of oxidative dehydrogenation and acceleration of formation of aromatic structure.

Samples of material being investigated in the form of those interwoven of 24 threads cords were consecutively subjected to heat treatment at temperatures from 20 to 1600° through are each 50-100° in furnace with tube graphite heater, which ensures possibility of isothermal heating in zone with length of 150 mm. The necessary temperature and the rate of heating furnace were set to by means of a regulator of load stress ROT-25/05 with the accuracy of $\pm 5^\circ$. Temperature to 1000° measured with laboratory platinum-rhodium- by platinum thermocouple, and in the interval of 1000-1600°-thermocouple of the type TBGG-066 with the pliable graphite electrodes. In the working zone of furnace 30 samples with a length of 150 mm, with a weight of 40-80 mg were placed simultaneously.

Up to 350° samples of initial material were heated at a rate of 0.5 deg/min in the atmosphere of air, and further to 1600° - in argon with a velocity of 50 deg/min. At 200 and 235° were accomplished/realized the isothermal holdings with duration to 20 hours each.

For studying process of thermal degradation with successive heat

treatment are applied methods of determining weight losses of, electron paramagnetic resonance (EPR), IR- spectra and measurement of resistivity of cord samples PAN.

Spectra EPR were removed/taken on standard spectrometer of type PE-1301, and vibrational spectra - on double-beam spectrograph IKS-14. In the latter case the samples were prepared by crushing fiber with the subsequent abrasion. The obtained powder-like samples were pressed into tablets with KBr.

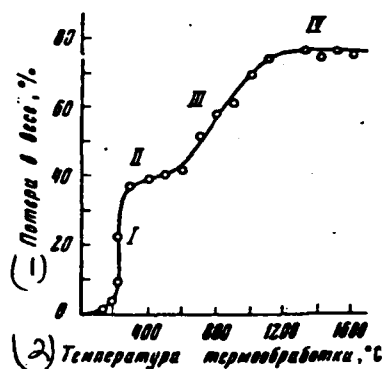


Fig. 1. Change of weight losses of an PAN-fiber depending on temperature of heat treatment (TTO).

Key: (1). Losses in weight, %. (2). Temperature of heat treatment, °C.

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Electrical resistance of heat-treated samples was measured according to compensation diagram. For calculating specific electric resistance, was measured the diameter of monofilament (on *MIM-7* microscope) and they determined the cross-sectional area of cord.

Fig. 1 shows change in losses in the weight of the samples investigated in dependence on temperature of heat treatment (TTO) in interval of 20-1600°. The obtained curve reflects the course of the pyrolysis of a PAN-fiber, which is characterized by a sharp variation of the rate of process in the dependence on its conditions in different temperature intervals of processing/treatment. In the course of the process are revealed four characteristic stages:

I - 20-300° - low- temperature pyrolysis, which takes place with the maximum rate in temperature interval of 235-300°, II - 300-600° - moderating region of pyrolysis; III - 600-1100° - mean temperature stage, which is characterized by the large output/yield of decomposition products, IV - 1100-1600° - high-temperature stage of retarding/deceleration and stop of thermal decomposition.

Specific presentation/concept about character of structural conversions of PAN during the first stage of pyrolysis it is possible to compose on the basis of the analysis of the IR-spectrum of initial specimen (Fig. 2a) and of those heat-treated up to 200, 235 and 250° with application of isothermal holdings (Fig. 2b). The comparison of curves shows that already after heating up to 200° with the five-hour aging in the material occurs the formation of conjugated double bonds - strip 1585 cm^{-1} appears. Since the characteristic for $\text{C}=\text{N}$ -bond strip 2240 cm^{-1} in the initial material remained constant and after its heat treatment, it is possible to assert that in this case are formed not $\text{C}=\text{N}$, but the $\text{C}=\text{C}$ -conjugated bonds. The intensity of strip 2240 cm^{-1} somewhat is reduced after 20-hour aging at 200° and is more noticeable at 235° during aging for 20 hours and also further at 250°. Occurring in this case increase in the intensity of strip 1585 cm^{-1} is conditioned on formation both $\text{C}=\text{C}$ and $\text{C}=\text{N}$ -conjugated bonds.

Thus, during oxidative dehydrogenation of PAN in stage of low-temperature pyrolysis simultaneously with sharp increase in weight losses of are provided conditions for accelerated formation of

aromatic structure. The initial material is gradually converted into the intermediate product qualitatively new by the chemical composition and according to the structure, for which characteristically very weak decomposition and respectively low weight losses of at the second stage of process - in the range of 300-600°. The represented in Fig. 3 and 4 dependences, which show an increase in the concentration of paramagnetic centers (PMTs) and lowering of specific electrical resistance, beginning with 400° they testify about further post of the chains of conjugation at this stage of temporary/time stabilization of thermal decomposition of material.

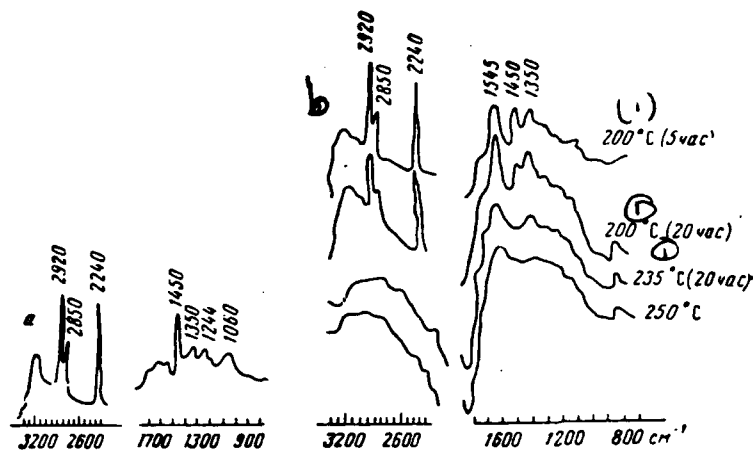


Fig. 2. IR spectra of a PAN-fiber: a - initial, b - heat-treated up to 250° with aging in air at 200 and 235°.

Key: (1). hour.

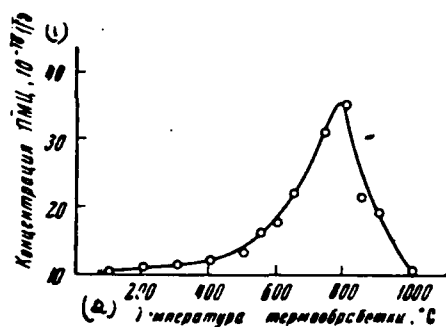


Fig. 3. Dependence of concentration of PMTs of samples of PAN-fiber on temperature of heat treatment.

Key: (1). Concentration. (2). Temperature of heat treatment.

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Very significant for third stage of process - in region of 600-1100° - is equally intensive change of shape of the curve of weight losses of, specific resistances and concentrations of PMTs. To

strengthening of thermal degradation of the obtained carburized product with dual conjugated bonds here corresponds a sharp reduction in the specific resistance (almost by 10 orders), achievements of the maximum of concentration of PMTs at 800° and subsequent steep/abrupt decreases to 1000°. It is possible to propose that in this region as a result of association of separate aromatic chains of conjugation the formation of plane carbon grids [lattices], which is accompanied by the intensive liberation/precipitation of the gaseous and liquid products, which are generated during the destruction of the uncycled sections of chain, begins. This is supported also by the shown in Fig. 5 course of changing the width of the line of signal EPR - ΔH . A noticeable decrease in ΔH up to 800° can be attributed to the exchange reaction, which is the result of an increase in the length of conjugation. However, the sharp increase in ΔH higher than 800° is caused by strengthening spin-lattice mechanism as a result of the appearance of a carbonic/carbon structure. A steep/abrupt decrease in the concentration of PMTs in the same section of TTO occurs due to a sharp increase in the quantity of current carriers with the formation of developed conjugated system [8].

Constancy of losses in the weight of heat-treated to 1100° PAN during its further heating up to 1600° (IV stage) testifies about complete completion of thermal decomposition.

According to available data [2], in composition of heat-treated to 1400° PAN nitrogen is no longer detected. Apparently, in

connection with this, in spite of the possible sealing/packing of material with TTO is higher than 1100° , its specific resistance it remains constant as a result of the disappearance of the high-conductivity conjugated double bonds $C=N$.

CONCLUSIONS

The experimental data, which characterize course of the process of thermal decomposition of PAN-fiber during heat treatment from 20 to 1600° with application of isothermal holdings in air in stage of low-temperature pyrolysis, are obtained.

It is noted that maximum increase in conjugated system, that is accompanied by formation of carbon structure, occurs in temperature interval of heat treatment at $600-1100^{\circ}$.

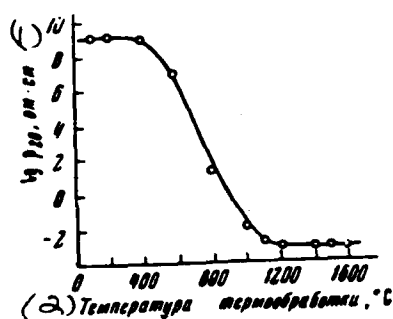


Fig. 4.

Fig. 4. Change in specific resistance of PAN-fiber during heat treatment from 20 to 1600°.

Key: (1). Ω·cm. (2). Temperature of heat treatment.

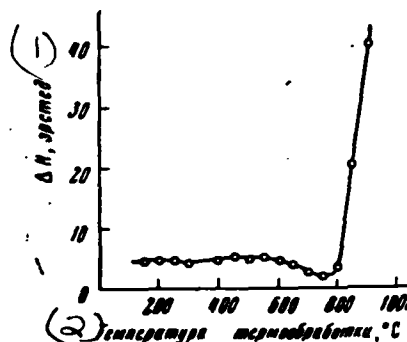


Fig. 5.

Fig. 5. Dependence of width of line of an EPR signal (ΔH) for samples of PAN-fiber on temperature of heat treatment.

Key: (1). oersted. (2). Temperature of heat treatment.

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